

# REPORT DOCUMENTATION PAGE

Form Approved  
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.

1. REPORT DATE (DD-MM-YYYY)

2. REPORT TYPE

Technical Papers

3. DATES COVERED (From - To)

4. TITLE AND SUBTITLE

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

5d. PROJECT NUMBER

2303

5e. TASK NUMBER

mlA3

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Air Force Research Laboratory (AFMC)  
AFRL/PRS  
5 Pollux Drive  
Edwards AFB CA 93524-7048

8. PERFORMING ORGANIZATION  
REPORT

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Air Force Research Laboratory (AFMC)  
AFRL/PRS  
5 Pollux Drive  
Edwards AFB CA 93524-7048

10. SPONSOR/MONITOR'S  
ACRONYM(S)

11. SPONSOR/MONITOR'S  
NUMBER(S)

12. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

20030110 068

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:

a. REPORT

Unclassified

b. ABSTRACT

Unclassified

c. THIS PAGE

Unclassified

17. LIMITATION  
OF ABSTRACT

A

18. NUMBER  
OF PAGES

19a. NAME OF RESPONSIBLE  
PERSON

Leilani Richardson

19b. TELEPHONE NUMBER

(include area code)  
(661) 275-5015

Standard Form 298 (Rev. 8-98)  
Prescribed by ANSI Std. Z39.18

13 separate items enclosed

TP-1998-087

2303M1A3

98-130

MEMORANDUM FOR IN-HOUSE PUBLICATIONS

FROM: PROI (TI) (STINFO)

26 May 98

SUBJECT: Authorization for Release of Technical Information, Control Number: AFRL-PR-ED-TP-1998-087  
Tim Haddad....Joe Lichtenhan "Thermoplastics Modified with Nanoscale Inorganic Monomers"  
Journal Submission (Statement A)

# THERMOPLASTICS MODIFIED WITH NANOSCALE INORGANIC MACROMERS

TIMOTHY S. HADDAD\*, PATRICK T. MATHER§, HONG G. JEON†,  
ANGEL ROMO-URIBE‡, AMY R. FARRIS†, JOSEPH D. LICHTENHAN†  
\*Raytheon STX, and †Air Force Research Lab, Edwards Air Force Base, CA 93524  
§Air Force Research Lab and ‡Systran Corp., Wright Patterson Air Force Base, OH 45433

## ABSTRACT

We have taken a unique approach to the synthesis and study of hybrid organic/inorganic materials. Our method involves synthesizing nano-size inorganic  $P_1R_7Si_8O_{12}$  clusters which contain seven inert "R" groups for solubility and only one functional "P" group for polymerization. This strategy permits the synthesis of melt processable, linear hybrid polymers containing pendent inorganic clusters and allows us to study the effect these clusters have on chain motions and polymer properties. The synthesis of norbornenyl-based polyhedral oligomeric silsesquioxane (POSS) macromers, their ring opening metathesis copolymerizations with varying amounts of norbornene, and analysis of the effect of the pendent POSS group is presented. The mechanical relaxation behavior and microstructure of norbornyl-POSS copolymers have been examined for their dependencies on the mole fraction of POSS-norbornyl monomer, as well as for potential sensitivity to the seven inert "R" groups present in each POSS macromer. POSS copolymerization is observed to enhance the  $\alpha$ -relaxation temperature,  $T_\alpha$ , in proportion to the mole fraction of POSS-norbornyl comonomer. Interestingly, however, the magnitude of this dependence is larger for POSS-norbornyl comonomer possessing cyclohexyl groups (CyPOSS) than for cyclopentyl groups (CpPOSS). While POSS copolymerization yields only slight enhancement of the tensile storage modulus measured near room temperature, at temperatures lower than a strong mechanical relaxation ( $\beta$ -relaxation near  $T = -75^\circ\text{C}$ ), there is a significant POSS-reinforcement of the storage modulus.

## INTRODUCTION

The design of new materials with enhanced properties continues to be a driver for the investigation of hybrid materials. As hybrid materials are copolymers based on inorganic and organic comonomers, they display enhanced properties by bridging the property space between two dissimilar types of materials.<sup>1</sup> A typical hybrid material will contain a crosslinked inorganic phase bound (often covalently) with an organic phase. Depending on the relative amounts of the two components, the properties of the resulting hybrid are intermediate between that of an inorganic and an organic polymer. Such methodology can be used to create either plastic inorganics or toughened plastics, and is superior to traditional blending methods.<sup>1b</sup> However, as most hybrid materials are obtained through a sol-gel type process, they tend to be highly crosslinked and difficult to process.

Our approach to the synthesis of easily processed hybrid materials is to design well-defined inorganic *oligomers* with only a single polymerization site per cluster. Each oligomeric cluster has an exactly defined degree of polymerization of eight,  $(RSiO_{1.5})_8$ , or more precisely,  $P_1R_7Si_8O_{12}$ . These polyhedral oligomeric silsesquioxane (POSS) macromers have an inorganic silica-like core and are surrounded by eight organic groups, of which seven are inert and just one is reactive. Polymerization at the single reactive "P" site, results in a linear polymer containing monodisperse, nano-size inorganic clusters<sup>2</sup> pendent to an organic polymer backbone<sup>3</sup>.

POSS systems have been the recent focus of much research in Air Force and other laboratories.<sup>3,4</sup> These materials feature potential for such applications as ablatives and thermal

DISTRIBUTION STATEMENT A  
Approved for Public Release  
Distribution Unlimited

protection (raised  $T_g$ ) of composite matrix resins. POSS has now been introduced into such thermoplastic resins as styryls, acrylics, liquid crystalline polyesters, siloxanes, and polyamides. Uniformly, it is observed that the glass transition temperature of the base resin is efficiently enhanced upon copolymerization with the associated POSS monomer. Additionally, we have reported on the modification of rheological properties of polystyrene/POSS copolymers, showing evidence for retardation of chain motion and group interaction effects.<sup>3g</sup> Of current interest, including the present work, is the determination of POSS modification of such solid-state properties as mechanical relaxation, fracture behavior, and abrasion resistance.

Recently, we have developed a hybrid POSS-norbornyl monomer by connecting a POSS to norbornene with an ethyl spacer. As with norbornene, this monomer can be polymerized using ring-opening metathesis polymerization (ROMP) catalysis. We have prepared a series of random copolymers of norbornene/POSS-norbornene for microstructural and mechanical relaxation investigations.

## EXPERIMENT

**POSS Macromers.** The two POSS macromers **1a,1b**,  $P_1R_7Si_8O_{12}$  with  $P = C_7H_9CH_2CH_2-$  (ethylnorbornenyl) and  $R = c-C_6H_{11}$  or  $c-C_5H_9$ , were both synthesized in the same manner from the known trisilanols<sup>5</sup>,  $R_7Si_7O_9(OH)_3$ , and the appropriate trichlorosilane,  $PSiCl_3$ . The synthesis and characterization of  $(C_7H_9CH_2CH_2)(c-C_6H_{11})_7Si_8O_{12}$ , **1a**, is given as a representative example. To a 200 mL THF solution of  $(C_6H_{11})_7Si_7O_9(OH)_3$  (21.19 g, 21.8 mmol) and triethylamine (7.27 g, 71.8 mmol) a slight excess of norbornenylethyltrichlorosilane (6.12 g, 23.9 mmol) was slowly added. The reaction flask was stirred under nitrogen for 12 hours, followed by filtration to remove the  $HNEt_3Cl$  byproduct. The product was isolated by concentrating the clear THF filtrate to 100 mL and then precipitating **1a** into rapidly stirred methanol (250 mL). The product was collected by filtration and dried in vacuo to yield 22.60 g of **1a** (93% yield). Elemental Analysis, Calculated (Found): %C 54.70 (54.70); %H 8.10 (8.44).

**Polymerizations.** The polymers were all synthesized under nitrogen using the ROMP catalyst<sup>6</sup>,  $Mo(C_{10}H_{12})(C_{12}H_{17}N)(OC_4H_9)_2$ , in chloroform with various proportions of norbornene and the two POSS-norbornenyl derivatives **1a** and **1b**. The polymerizations were designed to yield polymers with degrees of polymerization of 500 by controlling the ratio of monomers to catalyst. The reactions were terminated by addition of benzaldehyde. The polymers were precipitated and purified by adding the toluene solution to a large excess of methanol and collecting the precipitate. This resulted in random copolymers in yields over 90 %.

**Thermal Analysis.** The glass transition temperatures were determined using a TA Instruments differential scanning calorimeter (DSC). The temperature corresponding to the midpoint in the heat capacity step-rise is used for this purpose. The second heating run data are used with samples heated at a rate of 10 °C/min.

**Dynamic Mechanical Analysis** A Perkin Elmer DMA-7e was run in tensile mode at an oscillation frequency of 1 Hz with a static stress level of 5 105 Pa and a superposed oscillatory stress of 4 105 Pa. With this stress controlled instrument, the strain and phase difference between stress and strain are the measured outputs. Typically the resulting strain levels ranged from 0.05% to 0.2%. The typical sample dimensions were: 5 mm long, 0.5 mm wide and 0.2 mm thick. A gaseous Helium purge and a heating rate of 2 °C/min were employed. The temperature scale was calibrated with Indium and the force and compliance calibrations were performed following conventional methods.

## RESULTS

**Synthesis, Characterization and Polymerization of POSS Macromers.** The synthesis of POSS macromers containing a single norbornenyl group has been achieved by derivatizing the known trisilanols  $R_7Si_7O_9(OH)_3$ , ( $R$  = cyclohexyl or cyclopentyl).<sup>4</sup> These trisilanols are quantitatively "corner capped" with norbornenylethyltrichlorosilane in high isolated yields (Figure 1). The resulting macromers **1a-1b** have a spherical ( $Si_8O_{12}$ ) inorganic core, surrounded by seven inert alkyl groups for solubility and one reactive norbornene group for polymerization. These two similar macromers allow us to synthesize and compare polymers which differ only by the inert "R" groups on the POSS cage.

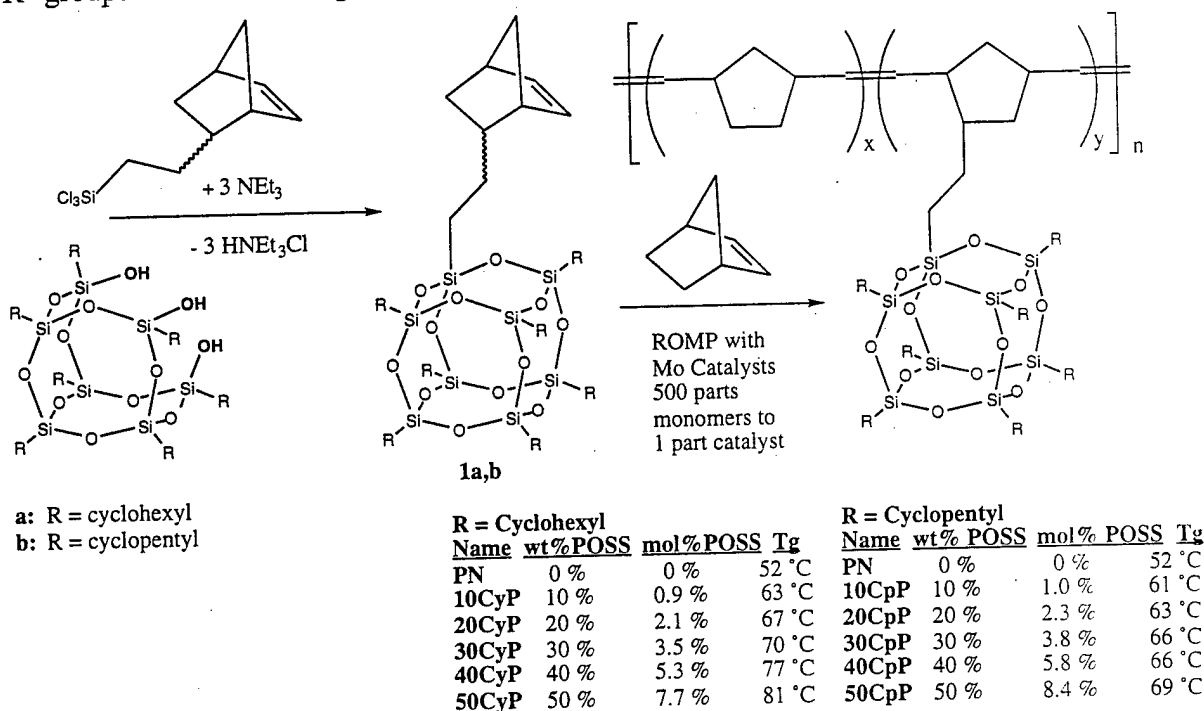


Figure 1. Polymerization of POSS-norbornene macromers with norbornene.

Random copolymers of norbornene and either of the two POSS macromers **1a-1b** were prepared by carrying out Molybdenum catalyzed ring opening metathesis polymerizations; the polymerizations were designed to yield polymers with a degree of polymerization of 500. These polymers may be viewed as organic polymers filled with monodisperse inorganic particulate which are covalently bound to the polymer backbone. Figure 1 summarizes the reaction scheme, the nomenclature used to identify the polymers in the text, the weight and mole % POSS in each polymer, and the glass transitions as measured by DSC.

**Dynamic Mechanical Analysis** The mechanical properties of the poly(norbornene-co-norbornylCyPOSS) and poly(norbornene-co-norbornylCpPOSS) copolymers, termed %CyP and %CpP, respectively, were determined using dynamic mechanical testing in tensile mode over a wide range of temperatures. In order to demonstrate the salient features of our observations, we first present a comparison of the polynorbornene homopolymer, PN, with 50CyP and 50CpP, followed by a presentation of the data for a range of POSS weight percentages. Shown in Figure 2 are the storage and loss tensile moduli versus temperature for (a) PN (b) 50CpP, and (c) 50CyP, where the oscillation frequency is 1 Hz. Several changes to the mechanical properties are observed to result from copolymerization of 50 weight % POSS in polynorbornene. First, we observe the appearance of a strong mechanical relaxation, here termed  $\beta$  relaxation, at  $T = -78$  °C

in **50CyP** not observed in the **PN** homopolymer, nor in the **50CpP** copolymer. For temperatures below this relaxation, the storage moduli for all three polymers are quite comparable, though with slightly different temperature dependencies. However, above  $T_\beta$  (the temperature corresponding to the  $\beta$  transition) the modulus of **50CyP** drops to values just under that of the **PN** homopolymer, while the modulus of the **50CpP** copolymer remains higher than that for **PN**. This strong dependence of the modulus profile on the POSS R-groups strongly suggests the involvement of the R-group in the  $\beta$  relaxation for the **50CyP** copolymer. ✓

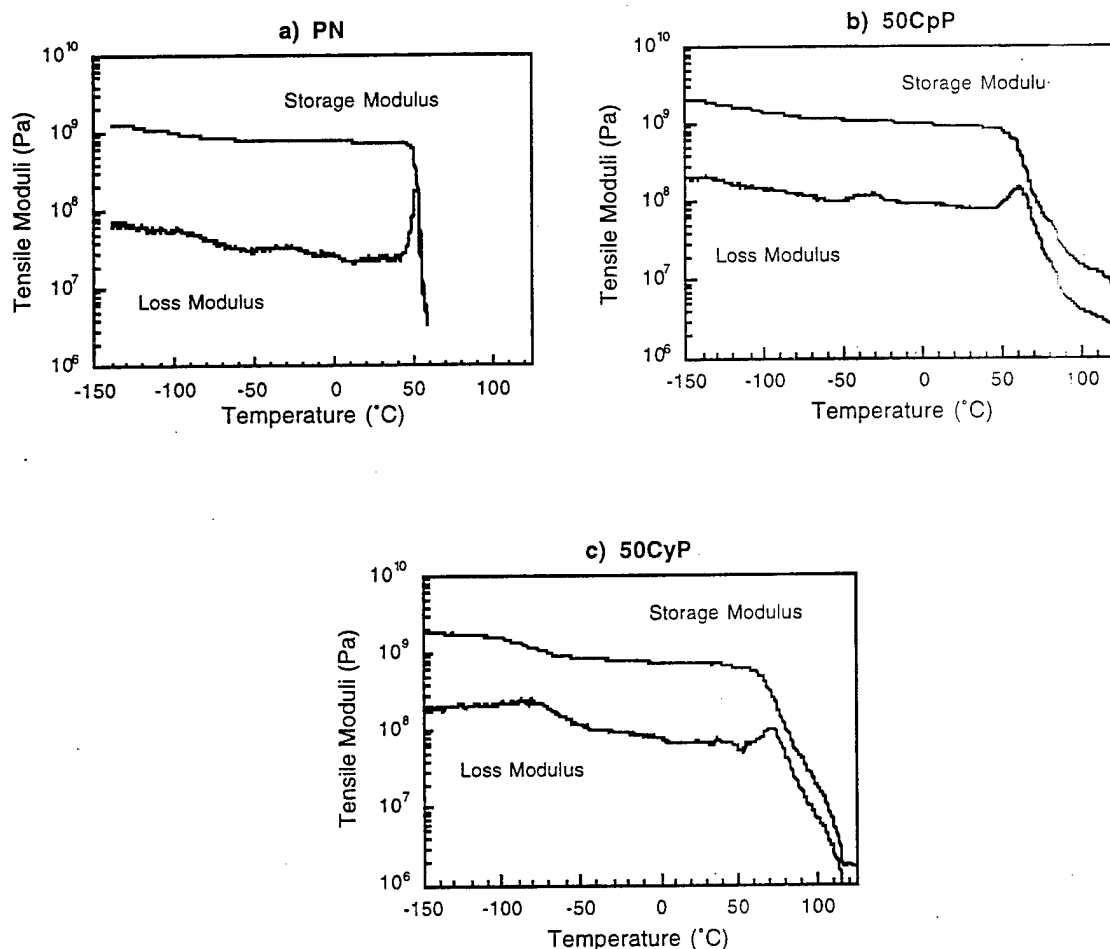


Figure 2. Storage and loss modulus vs temperature for a 1 Hz linear stress oscillation on POSS-polynorbornenes: a) 0 % POSS, b) 50 weight % CpPOSS, c) 50 weight % CyPOSS.

A second observation from Figure 2 is the dependence of the temperature of the primary mechanical relaxation peak in the tensile loss modulus profile, referred to as the  $\alpha$ -relaxation, on the copolymerization with POSS.  $T_\alpha$  (the temperature corresponding to the  $\alpha$ -relaxation) is observed to increase approximately 25 °C for **50CyP** over **PN** and, in addition, the loss modulus peak broadens significantly. **50CpP**, on the other hand exhibits a more modest increase in  $T_\alpha$ , 10 °C, though with the same peak broadening observed with **50CyP**.

A final feature evident in the DMA traces of Figure 2 is an alteration in the temperature dependence of the tensile moduli above  $T_\alpha$  afforded by CpPOSS or CyPOSS copolymerization. While the moduli for the **PN** homopolymer quickly drop with temperature above  $T_\alpha$ , i.e., two decades over 10 °C, the same in drop in moduli for **50CyP** and **50CpP** takes place over a much ✓

larger temperature range of 50 °C. This alteration of the moduli profiles should translate to an increase in the heat deflection temperature larger than that indicated by the increase in the  $\alpha$ -transition temperatures. The origin of this type of alteration in DMA behavior is either: (i) modification of the rheological properties of the polymer in the molten state, or (ii) morphological modification such as the introduction of crystallinity due to POSS copolymerization. Because the shape of the relaxation peaks for  $T_\alpha$  in Figure 2(b) and 2(c) are largely symmetric, rather than biased to higher temperatures, we favor the rheological hypothesis. Some precedent for the modification of polymer rheology with POSS copolymerization has been reported<sup>3g</sup> and is likely active in this system, a subject of our current research efforts.

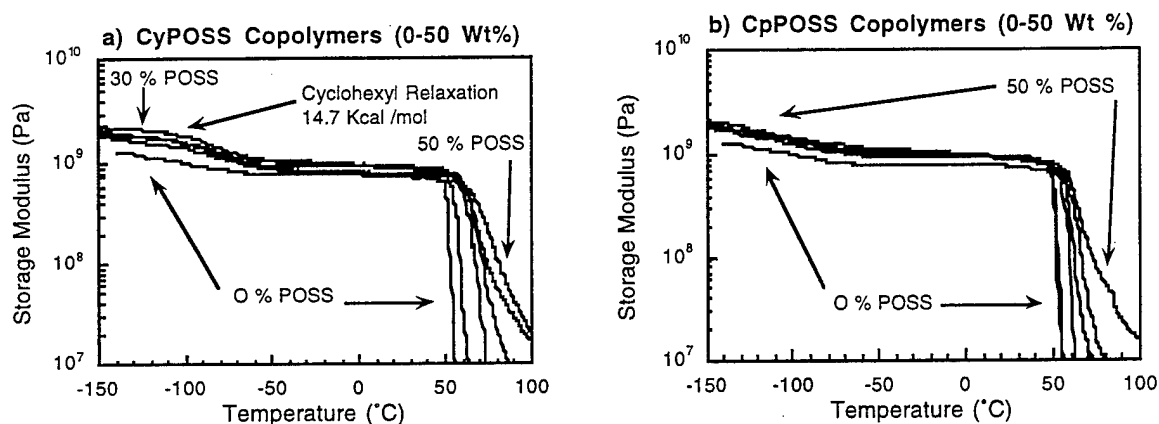


Figure 3. Storage tensile modulus vs temperature for a series of CyPOSS copolymers (a) and CpPOSS copolymers (b) with increasing weight % of POSS comonomer from 0 to 50 %.

Figure 3a shows a comparison of the tensile storage moduli traces for the *n*CyP copolymers with *n* values of 0, 10, 20, 30, 40 and 50 weight percent. The modest tensile modulus values are not dramatically affected by copolymerization with CyPOSS, showing a slight increase, then a decrease, with increasing POSS content. Values of the tensile moduli near room temperature range from 1.1 GPa to 0.8 GPa. On the other hand, the tensile moduli for temperatures lower than  $T_\beta$  are clustered near a value of 2 GPa, with a maximum modulus for the 30CyP copolymer apparently arising from the large magnitude of the  $\beta$ -transition. Also apparent from figure 3a is the shift in the  $\alpha$ -transition toward increasing values with increasing weight percentage of POSS, along with a systematic decrease in the drop-off in modulus with increasing temperature as discussed above for the 50CyP copolymer.

The mechanical relaxation behavior of the CpPOSS copolymers has also been examined and the results are plotted in Figure 3b. It is seen from the plot of tensile storage modulus versus temperature that the modulus features a strong decrease with increasing temperature for temperatures over about 50 °C. Figure 3 also reveals a monotonic dependence of the modulus on CpPOSS weight percentage at any given temperature.

## CONCLUDING REMARKS

The synthesis of soluble, thermoplastic hybrid materials from well-defined inorganic clusters containing only a single polymerization site has been developed. Two norbornenyl-based POSS derivatives were successfully copolymerized with norbornene and analysis of the resulting copolymers revealed some interesting trends. The mechanical relaxation behavior and

microstructure of norbornyl-POSS hybrid copolymers have been examined for their dependencies on the mole fraction of POSS-norbornyl monomer, and have been found to be sensitive to the seven organic corner groups present in each POSS macromer. POSS copolymerization is observed to enhance the  $\alpha$ -relaxation temperature,  $T_\alpha$ , in proportion to the mole fraction of POSS-norbornyl comonomer. Interestingly, however, the magnitude of this dependence is larger for POSS-norbornyl comonomer possessing cyclohexyl groups than that with cyclopentyl groups. While POSS copolymerization has only a slight effect on the tensile storage modulus measured near room temperature, at temperatures lower than a strong mechanical relaxation ( $\beta$ -relaxation near  $T = -75^\circ\text{C}$ ), there is a significant POSS-reinforcement of the storage modulus. The position of the  $\beta$ -relaxation observed in the CyPOSS series of copolymers is independent of POSS mole fraction, and the frequency dependence of this peak position yields the activation energy,  $\Delta H_\beta = 14.7$  kcal/mol. It is concluded that this relaxation arises from the onset of free rotation of the cyclohexyl groups. A similar effect is observed, in part, for the CpPOSS copolymers, although only part of the relaxation can be observed. Therefore we conclude that the POSS nanoscale filler is responsible for modifying the observed modulus behavior.

#### ACKNOWLEDGMENTS

This research was supported by the Air Force Office of Scientific Research, Directorate of Chemistry and Life Sciences, and the ~~Phillips~~ Laboratory, Propulsion Directorate.  
Air Force Research

#### REFERENCES

1. Reviews and leading references for recent progress in hybrid materials are: (a) Hybrid Organic-Inorganic Composites, edited by J.E. Mark, C.Y.-C. Lee and P.A. Bianconi, (ACS Symposium Series **585**, American Chemical Society: Washington DC 1995). (b) L. Mascia, Trends Polym. Sci. **3**, 61 (1995). (c) C. Sanchez and F. Ribot, Nouv. J. Chem. **18**, 1007 (1994).
2. The diameter swept out by a  $\text{R}_8\text{Si}_8\text{O}_{12}$  POSS molecule is approximately 15 Å with an inner Si—Si diameter of 5.4 Å. (a) K. Larsson, Ark. Kemi, **16**, 203 (1960). (b) F.J. Feher and T.A. Budzichowski, J. Organomet. Chem. **373**, 153 (1989). (c) T.P.E. Auf der Hyde, H.-B. Burgi, H. Burgy and K.W. Tornroos, Chimia, **45**, 38 (1991)
3. (a) J.D. Lichtenhan, N.Q. Vu, J.A. Carter, J.W. Gilman and F.J. Feher, Macromolecules, **26**, 2141, (1993). (b) J.D. Lichtenhan, Comments Inorg. Chem. **17**, 115 (1995). (c) T.S. Haddad and J.D. Lichtenhan, J. Inorg. Organomet. Polym. **5**, 237 (1995). (d) J.D. Lichtenhan, Y.A. Otonari and M.J. Carr, Macromolecules **28**, 8435 (1995). (e) R. Mantz, P.F. Jones, K.P. Chaffee, J.D. Lichtenhan, J.W. Gilman, I. Ismail and M.J. Burmeister, Chem Mater. **8**, 1259 (1996). (f) T.S. Haddad and J.D. Lichtenhan, Macromolecules **29**, 7302 (1996). (g) P.T. Mather, A. Romo-Uribe, T.S. Haddad, and J.D. Lichtenhan, J. Polym. Sci. Part B: Polym. Phys. *In Press* (1998).
4. C.X. Zhang and R.M. Laine, J. Organomet. Chem. **521**, 199 (1996).
5. (a) F.J. Feher, D.A. Newman and J.F. Walzer, J. Am. Chem. Soc. **111**, 1741 (1989). (b) F.J. Feher, T.A. Budzichowski, R.L. Blanski, K.J. Weller and J.W. Ziller, Organometallics **10**, 2526 (1991). (c) J.F. Brown Jr. and L.H. Vogt Jr. J. Am. Chem. Soc. **87**, 4313 (1965).
6. G.C. Bazan, E. Khosravi, R.R. Schrock, W.J. Feast, V.C. Gibson, M.B. O'Regan, J.K. Thomas and W.M. Davis, J. Am. Chem. Soc. **112**, 8378 (1990).